

# Chapter Thirteen

## RESIDUE & ENVIRONMENTAL SAMPLES

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# RESIDUE AND ENVIRONMENTAL SAMPLES

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## INTRODUCTION

This chapter was developed to aid field personnel in the collection of samples during pesticide incident investigations. Sometimes sampling is done to establish hazardous areas such as accidental spills, or to show that a pesticide was applied to a site not on the label, or to show that, during application, a pesticide reached a nontarget site prohibited by the label. Physical evidence is often used to support a case involving alleged violations of pesticide laws. The investigator must collect and submit samples of physical evidence using methods that ensure the integrity of the evidence. This will include information gathering, setting of sample goals, and formulation of a sampling plan. Investigators should use this section to provide direction in their sampling procedures and as a reference in unfamiliar situations.

In many investigations the decision to collect samples must be made immediately. Suspected human, animal, crop, or environmental contamination can require quick action to determine exposure or to prevent contaminated commodities from entering the food chain. Pesticides that degrade quickly will require sampling soon after their application to detect their presence. At some point in the information gathering process, the investigator may realize that immediate sampling is essential if the resulting analysis is to be meaningful to the investigation. When in doubt, it is preferable to take as many samples as could be needed and to select those which are appropriate for analysis at a later time.

There are certain responsibilities the investigator must consider during the investigation. Samples are an important aspect of an enforcement action, but are only part of the overall information gathering process. Samples cannot take the place of good investigative procedures. The investigator must determine the goal of the sampling and the appropriate sampling methods which correspond to the goal. The nature of the incident will largely

define the investigator's goals and the sampling goals will direct the way samples are taken. The investigator's goal is to collect the appropriate type of samples to support an investigation of alleged violations. In some investigations, sampling or sample analysis may not be justified if enough time has elapsed to allow degradation of suspected materials.

The investigator must gather as much background information as possible. Cropping patterns, a history of pesticide use, technical data on the pesticide formulation(s), application methods, and weather conditions at the time of the incident are some of the factors to be considered in determining sampling procedures. The investigator must be aware of his/her laboratory's capabilities. Some pesticides may require special sampling techniques or handling procedures to ensure accurate analysis. For example, collection of specific plant parts may be required with certain formulations. Proper storage and transportation of samples is critical and can affect the analysis results. It is important to coordinate sampling activities with the laboratory and follow their procedures to ensure the integrity of the sample is maintained.

Once background information has been assembled, a sampling plan must be formulated. The plan must account for sampling equipment, sampling procedures, amount and location of each sample, safety precautions, quality assurance requirements, storage, and method of transportation. At the incident site, the investigator must conduct a preliminary survey of the area. This will help locate landmarks, determine the objective of sampling, and facilitate questioning of witnesses. A sketch or diagram of the immediate area with landmarks, location of witnesses, measurements, points of compass, and location of samples is mandatory for all thorough investigations. Photographs can be helpful in documenting crop maturity and surrounding landmarks (see Chapter One - Documentary Support). Field notes must be taken with enough detail to prepare a complete written report later. Information from parties involved and witnesses is more accurate if gathered soon after the incident. Supportive evidence (i.e., labeling, use reports, etc.) is important where available. Maintain the Chain of Custody with all physical evidence. Finally, draw all the elements of the investigation together to prepare the investigative report.

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## SAMPLING PLAN

If the goals of the investigation require sampling, then a sampling plan must be developed. For the more experienced investigators, this thought process is initiated as soon as they are informed of the incident and continues until samples are collected. The sampling plan can be a thought process or a "formal" written outline. The sampling plan outline is intended to be used as a reference and training guide for new or less experienced investigators, but should be reviewed periodically to refresh the memories of all investigators.

Prior to sampling, consider distances and physical surroundings at the incident site. Review notes, statements, permits, use reports, and technical data on the alleged pesticides used to develop a sampling plan. Because of time constraints and priorities, it will probably not be possible to address all the items listed. It is imperative, however, to establish the sampling goals before collecting samples.

## Review Evidence

The first step in developing a sampling plan is to review the evidence gathered during the initial phases of the investigation. Statements and interviews are an integral part of the investigation. They will assist in determining the type of incident, validity of the complaint, priority of the case, the pesticides used, the method of application, approximate distances between treatment site(s) and incident site, weather conditions, date and time of application(s), application pattern, illness symptoms, crop damage patterns, etc.

## Obtain Technical Data From Various Sources

### Pesticide(s)

Technical data will assist in determining sample types, methods and location, a time frame in which to collect samples, and if there should be any special handling or sample preparation procedures. Refer to the *Farm Chemicals Handbook, Crop Protection Chemicals Reference, Pesticide Product Description* (section 18, "Toxicology") or contact the supervisor to assist in gathering this information.

- < Chemical properties
  - Formulation
  - Half-life
  - Metabolites
- < Physiological and biochemical behavior
  - Foliar absorption characteristics
  - Translocation action
  - Behavior in or on soils
- < Absorption and leaching characteristics
  - Microbial breakdown
  - Loss from photodecomposition and volatilization
  - Hydrolysis
- < Toxicological properties
  - Toxicity to humans/wildlife/fish
  - Acute/chronic toxicity
  - Poisoning symptoms
- < The laboratory capabilities

- Method of analysis
- Analytical sensitivity
- Availability of method and/or reference standard(s)

### **Weather Data**

Weather data (at time and place of incident occurrence), if available, will help in determining drift patterns, volatilization rates, off-target movement of pesticides, etc. This information can be obtained from the National Weather Service, local agencies, airports, etc.

- < Wind speed and direction
- < Rainfall
- < Temperature
- < Inversion
- < Humidity

### **Sample Selection**

Selecting the sample type(s) will depend on the type of incident that allegedly occurred. For example, if the incident involved:

- < Drift of a pesticide on people, the sample type could include total foliage. (i.e., total residue on foliage) in a gradient pattern and surface clothing.
- < Drift of pesticide on people harvesting a commodity, the sample types may include total foliage in gradient pattern, total commodity, dislodgeable foliage and surface clothing.
- < Misuse of a pesticide in a structure (e.g., crawlspace), the sample types may include total soil and surface (wipe).
- < Crop damages from run-off containing a pesticide sample types may include total soil or total foliage in a gradient pattern, total commodity and total plant.
- < Fumigation of railcars, ships, containers or homes.

In most drift incidents, the pesticide application in question has been performed a short time before. If the available plants have a heavy canopy, thus allowing limited soil exposure to direct spray, vegetation should be chosen as the sample of choice. If vegetation at the incident site is limited, excessive time has passed since the application, there is new plant growth or heavy rains could have reduced the concentration, soil should be the sample of choice.

The purpose of sampling is to collect evidence to determine if a violation occurred. An investigator will have to use his/her best judgment in selecting the appropriate sample types based on the information gathered.

Whatever sample type is used, samples must be representative of the media being sampled if it is to provide the basis on which to determine that a violation exists. Therefore, a “statistical” approach

must be considered. This requires the selection of sampling points that will produce a representative sample (i.e., non-point grid pattern). In addition, keep in mind the statistical considerations that affect representative sampling, such as variability in sample collection methods; frequency of samples taken over a period of time; and number of samples collected relative to size of site.

### Laboratory Reporting of Sample Types

Sample results, as reported by the laboratory, normally are reported in terms of:

- < Total (weight of pesticide/total weight of sample, ppm)
  - Foliage
  - Commodity
  - Plant (whole or portion)
  - Soil (surface or depth)
  - Animal/fish/honeybees
  - Water
  - Feed
  - Tank mix
  - Pesticide information (reported in percent)
- < Dislodgeable (weight of pesticide/surface area, : g/cm<sup>2</sup>)
  - Foliage
- < Surface (weight of pesticide/sample : g or wt/area, : g/cm<sup>2</sup>)
  - Clothing
  - Surface area
    - Windows
    - Rugs
    - Floors
    - Walls
    - Automobiles
- < Volume (weight of pesticide/volume, mg/m<sup>3</sup>, : g/l)
  - Air
  - Water

### Sampling Equipment

Unless disposable sampling equipment is used, the sampling equipment must be cleaned between each sample, using distilled water. To decontaminate the equipment, wash and double rinse with distilled water, then rinse with propyl or isopropyl alcohol (Note: Sulfonyl urea products require a 5% solution of chlorine for 1 minute contact time for decontamination). Also be sure to wash

your hands and change disposable gloves to prevent cross-contamination of samples. The equipment must be stored in the office or car, in a clean (i.e., uncontaminated) designated location. For smaller equipment, an enclosed, airtight container is recommended. The larger equipment can be wrapped in an uncontaminated cloth or cleaned and decontaminated prior to sampling.

### Sampling Equipment List

- < Sample Collection Record Forms.
- < Paper, plastic bags, jars (various sizes) and aluminum foil.
- < Personal safety equipment and clothing as required for sample collection (coveralls, respirator, goggles, hard hat, disposable & rubber gloves, boots, rain suit, waders, etc.).
- < Labels, tape, stapler, evidence tags, official seals or evidence tape.
- < Shovel, hand spade, knife, pruning shears, trowel, spatula, or leaf punch.
- < Hexane, isopropyl alcohol, distilled water, and paper towels.
- < Sterile wipes and precut templates. Measuring tapes, stakes, camera, film and accessories.
- < Ice chests (coolers, styrofoam), "Blue-Ice," wet ice, dry ice (Caution: *do not* handle dry ice with bare hands or allow samples to directly contact the dry ice).
- < Permanent markers, pencil, pen, note pad, record book.
- < County or city map, aerial maps, topographical maps.
- < Disposable core tubes, siphon tubes.

### Incident Site

Actual surveillance of the incident site, along with the evidence collected, will help provide a complete picture of what occurred. It will assist in determining whether possible violations occurred. It should be the basis for drawing a diagram of the incident site with specific landmarks to assist in the investigation. A Global Positioning System (GPS) device may be used to pin-point exact locations. Note: when surveying the incident site, ***do not*** contaminate yourself by walking through the treated area.

Make the following observations, as appropriate:

- < Distances from treatment site(s) (Note: the inspector should indicate if the diagram is not to scale, or if it is to scale, indicate the scale).
- < Odors in structures
- < Crop type, maturity, acreage
- < Physical surroundings

- Telephone poles (Note the ID # on the pole) adjacent crops
  - Sampling medium (foliage, surface areas, etc.)
  - Landmarks
  - Waterways
  - Location of workers
  - Vehicles
  - Trees
- < Physical evidence
- Crop/plant damage
  - Tire tracks
  - Spotting on leaves, walls, floors, etc.
  - Pesticide containers in storage

#### < Incident Site Diagram

After reviewing the evidence collected, (e.g. statements, interview notes, and records); surveying the incident site; researching and obtaining technical data on the pesticides allegedly used; and selecting the sample types; it is helpful to draw a diagram of the incident site as near to scale as possible with North at the top. Include the location of the incident site and treatment site (if different), landmarks, the crop's stage of growth, acreage, adjacent crops and sites, room dimensions, the location of witnesses, distances between the points, wind direction and speed. As samples are collected, identify their location(s) and distances on the diagram. The diagram must be large enough to include all of the details and be legible. Accurately identify locations of samples through triangulation (GPS can be used to accurately establish exact locations).

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## GENERAL SAMPLING GUIDES

Applying the following guidelines to individual cases will reduce haphazard sampling. Investigators must:

- < Adapt a sampling plan to the requirements of the individual investigation.
- < Have the necessary sampling tools and sample containers and personal protective equipment.
- < Always wear protective clothing and safety equipment as required by the pesticide label when entering treated fields/areas or handling samples.

- < During all phases of the investigation, be careful not to contaminate yourself or cross-contaminate the samples. Always wear clean disposable gloves, protective clothing, and safety equipment as required by the pesticide label, regulations, and policy when entering fields/areas or handling samples. It may be necessary to change gloves and other protective clothing between collecting each sample in order to help ensure that cross-contamination does not take place.
- < Concentrate sampling in the area that best manifests the symptoms associated with the problem. Different types of sample analyses (such as soil vs. grass) are difficult to compare. Similar materials should be used for comparison samples, such as in cases where treated and non-treated areas are to be compared. Similar foliage types (grass-to-grass) must be sampled when possible.

If the situation dictates, a composite, duplicate or split sample may have to be taken to meet the sampling objectives.

- < Composite Sample: Combination of two or more sub-samples to produce a homogeneous sample.
- < Duplicate Sample: Two or more samples collected from the same area subject to comparable conditions.
- < Split Sample: Division of a sample into two equal and identical portions. This is usually done at the laboratory.

Composite sample analyses must only be conducted when the area, crop, or material is suspected to be uniformly contaminated, to identify suspected chemicals, or to determine if a broad area is contaminated.

Draw a diagram of the incident site. The diagram must include such things as the sample locations, landmarks, adjacent crops and sites, room dimensions, the location of witnesses, distances between points, etc.

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## SAMPLE COLLECTION & PRESERVATION

Physical pesticide sampling may include concentrated pesticide formulations, diluted pesticide solutions, and any substance or material suspected to be contaminated (environmental residue samples). The following guidelines must be followed:

### Sample Containers (Guidelines)

All samples collected in glass (except one liter amber water samples) must be identified with the sample number, date, and inspector's initials and placed in large 12" x 30", inverted, heavy polyethylene bags. All samples collected in large 12" x 30" heavy polyethylene bags, must be sealed as follows:

(Note: evidence bags may also be used; however, they must be properly identified and sealed as appropriate).

- < Identify and officially seal samples immediately. Each container must be further identified with the sample number and inspector's initials. Place the sample(s) in the inverted polyethylene bag, and:
  - Twist the top of the bag, and tie a knot in the inverted bag.
  - Fold the top of the bag down over the knot and twist the bag around the knot.
  - Apply several wraps of tape (masking, monofilament, etc.) below the knot.
  - Apply the EPA Official Sample Seal (EPA Form 7500-2) (or if State/tribal inspection, the equivalent State Tribal Sample Seal) around the tape. The official sample seal shall be identified with the sample number, date, city, State of collection, and the inspector's name and signature.

For one Liter Amber Bottles:

- < Tape (masking, mon-filament, duct or equivalent type) individual dry bottles around the cap and deep into the neck.
- < Place investigator's initials across the end of the tape.
- < Follow all other procedures above for identifying, logging, and sealing the sample.

### Sample Collection Record (Guidelines)

A Sample Collection Record must be filled out in indelible ink and accompany the samples to the laboratory. The record must be placed in a separate sealed plastic bag to prevent moisture absorption.

- < Identify sample material as accurately as possible.
- < If possible, identify specific pesticides or classes (e.g., organophosphates, phenoxy, etc.) suspected to have caused the problem. Also include the phrase "WARNING-PESTICIDES" on the Sample Collection Record to warn laboratory personnel.
- < Identifying numbers on sample containers must be copied exactly as on the Sample Collection Record to identify the sample for the lab.

### Foliage

Pesticide drift or other misapplications of pesticides are often documented by sampling and analyzing foliage or whole plants for residues. The sampling techniques described below are applicable for most agricultural crops as well as nonagricultural vegetation

(non-crop) where suspected drift or overspray (swath displacement) is to be documented.

### **Discrete Foliage Sampling**

Samples may be collected in a gradient or grid pattern.

Collect foliage from a specific area (i.e., reference point) in the field. The purpose of collecting the sample from a specific area is to identify a residue delineation between the sample areas, and to maintain sampling uniformity. It is important to identify the location of the sample site within the field because the sample and incident site diagram may be used as evidence in an administrative or judicial action. The size of the sample area will vary with the type of location. For example:

- < At all sites, a control sample must be collected from an area of similar vegetation type as of that within the affected areas. It can be on the complainant's property, some distance away from the area treated and where drift/overspray is suspected. This sample is taken to verify that good sampling techniques were used and the sample was not contaminated. It is absolutely critical that the control sample be taken from an area known to be free of any contamination from the pesticides in question. A contaminated control sample will destroy the usefulness of other samples as evidence. Take only one substrate in each sample, i.e. soil only or vegetation only. They must not be mixed.
- < Subsequent samples must be collected in a sequential order from the least anticipated residue concentration to the greatest anticipated concentration, (i.e., control, suspected drift area, then target area). This will help reduce the potential for cross contamination of samples. Do not hesitate to take enough samples to show that drift occurred and to what extent by establishing boundaries of contamination. Unnecessary samples can always be discarded later by the lab. It is rarely possible to collect additional samples at a later time.
- < Field crops and non-crop areas (weeds, fallow fields, etc.): the size of the sample site must be approximately a 25-foot square (or 625 square feet).
- < Orchards and ornamentals: sample from approximately four mature trees/vines (rectangle or square area). The area will vary depending on the size of the incident site, the size of the plants and foliage within the site, and the number of samples intended to be collected.
- < Smaller plants (seedlings) with minimal foliage on a plant or tree (bud leaf stage), or multiple analyses: a larger area must be used.
- < Remember, measure the sample area and record it in the investigative notes.

- < Try to collect foliage of similar type (e.g., grasses or broadleaves only), if possible. It will make it easier to extrapolate the data. If similar type foliage is not available throughout the sampling area, collect different types of foliage.
- < Select foliage from all sides of the plant/tree unless drift is suspected. In this case, collect the foliage from the side of the plants allegedly exposed to the drift. For most situations, collect the foliage from the outer leaves of the plant/tree. It may be necessary to uproot the whole plant if systemic pesticide absorption is suspected. Do not select foliage that is in contact with soil. Only collect leaves; do not include twigs or branches. Remember, new growth not subject to chemical application may affect the results of an analysis.
- < Collect enough foliage from the specific sample area to permit proper analysis or screening. If composite, duplicate, or split samples are requested, increase the sample size accordingly. Contact the laboratory if in doubt regarding sample size.
- < Vegetation samples, etc. must be wrapped in aluminum foil (pre-rinsed with hexane) and placed in large 12" x 30", inverted, heavy polyethylene bags; alternately, vegetation samples can be collected in glass jars.
- < Use proper sample preparation and sample collection recording.
- < Indicate maturity of sample foliage, if applicable.
- < Samples must be chilled, refrigerated or frozen as soon as possible. An ice chest with regular or "Blue-Ice" can be carried into the field for this purpose. If samples are stored frozen, attempt to ship them on dry ice preventing the plant tissue from decomposing during shipment.
- < Samples must be shipped to the laboratory as soon as possible after they are collected.

#### ***Grid Pattern Foliage Sampling***

Grid pattern samples are taken to establish uniform or partial contamination of the incident site. The sampling pattern should represent the entire field or site. Each point on the grid represents a sample and should be kept separate from the others.

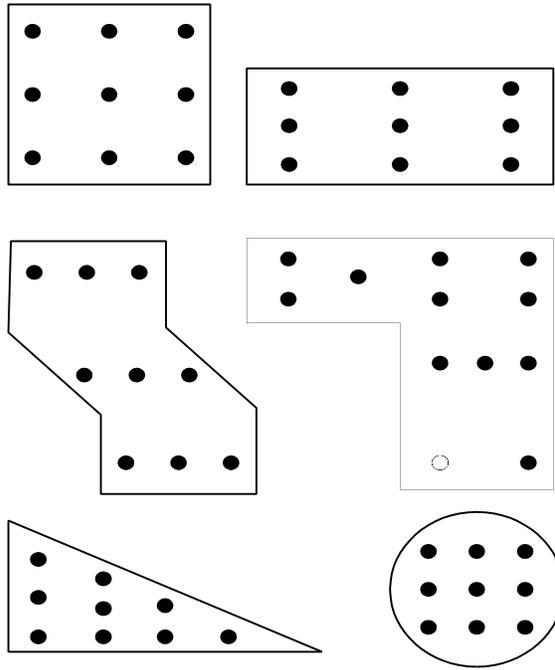


Figure 13-1: Grid Pattern Examples

If pesticide drift is suspected from an adjacent field or the source of contamination is unknown, a grid pattern may be used in place of the gradient pattern. If misapplication to part of a field is suspected (tank cross-contamination or partial application), but the treated area is unknown, this type of sampling pattern should be used to isolate the area (a GPS device may be beneficial in locating precise locations).

Collect samples in a grid pattern following the procedures indicated for a discrete foliage sample. Each sample represents one point on the grid for that field or site, therefore, do not composite them.

After a control sample is taken, the sampling grid pattern in the incident site must start approximately 100 feet from the edge of the field, depending on the field size. As a rule of thumb, the distance from the edges must represent approximately 10 percent of the width and length of the field or site. For example, a site 1,000 feet wide and 2,000 feet long (approximately 46 acres) has a starting point 100 feet in from the length and 200 feet in from the width. Each sample must be in line with, and at an equal distance apart from, one another in the grid pattern. Record the sample locations in the investigative notes and diagram(s).

If using the grid pattern to establish drift, collect one additional sample from each of the adjacent fields that are suspected of being the source of contamination.

Each foliage sample from a site must be of similar type and taken from the same location on the plant/tree. Identify the location and area from which each sample was taken on the diagram with distances from landmarks, field borders, and between samples clearly indicated.

Use proper sample preparation and Sample Collection Recording.

Gradient samples are taken to establish the severity and extent of a drift incident. After the control sample, always sample from an area of suspected lowest concentration in a direction towards the area of highest concentration (treatment site) to prevent contamination of samples. If more than one source of contamination is suspected, collect gradient samples towards each suspected source or use the grid pattern. Do not composite samples. Wear the required protective clothing and use clean, uncontaminated gloves and tools between each sample.

Samples must be collected from defined areas in the field or site similar to the methods indicated in the procedures described previously for a discrete foliage sample.

In most situations, collect a minimum of five foliage samples in a gradient pattern at an equal distance apart. At minimum, one control sample must always be from outside of the suspected contaminated area and at minimum, one sample must be from the suspected source area of contamination. The gradient pattern must be in a straight line.

Foliage must be of similar type and taken from the same location on the plant/tree for each sample. On the diagram, identify the location and area from which each sample was taken including distances from landmarks, field borders, and distances between samples.

Refer to Discrete Foliage Sampling for sample size, sampling sequence, containers, and sample preservation. Maintain the Chain of Custody.

Use proper sample preparation and Sample Collection Recording.

### **Composite Foliage Sampling**

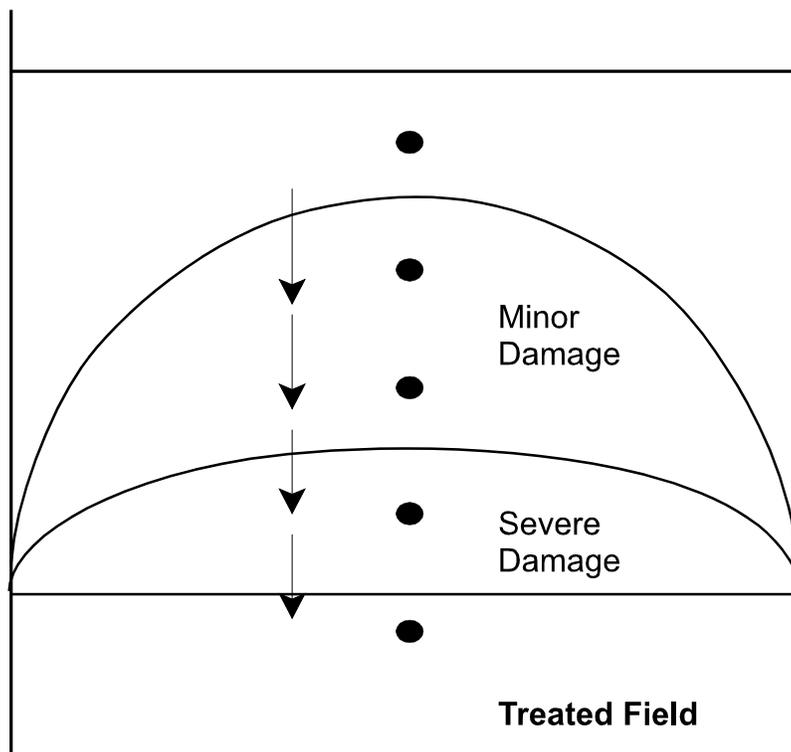
Composite samples are taken to determine whether or not an area is contaminated and to determine if other samples must be analyzed. After taking a control sample, a composite sample is made up of several sub-samples that are of equal volume or weight and are combined to represent a field or site. Collect enough foliage for each grid point sample to allow for the requested analyses.

### **Crop Damage Residue Incidents**

After taking a control sample, samples must be taken in a line, at approximately equal intervals, from non-suspected area to the target treated area. (Top to bottom).

***Human Exposure Incidents***

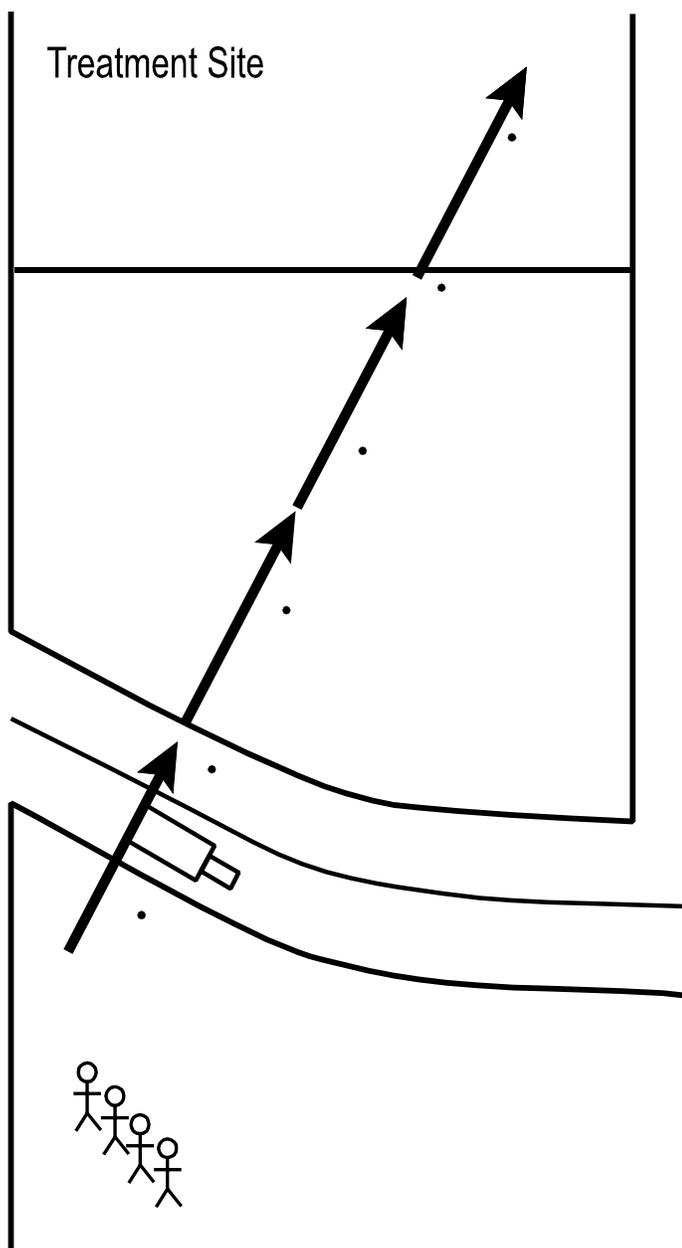
After taking a control sample, samples must be taken in a line, at approximately equal intervals, from the least-suspected area (near the children) to the target treated area. (Bottom to top).



*Figure 13-2: Gradient Sampling Diagram - Crop Damage Residue Incident*

***Sample Collection***

- < Wipe from vehicle
- < Vegetation/soil samples in gradient pattern
- < Clothing



*Figure 13-3: Gradient Sampling Diagram - Human Exposure Incident*

*Property Loss Incidents*

Sample Collection

- < Vegetation/soil samples in gradient pattern
- < Commodity, if harvesting
- < Wipes from vehicle

< Clothing

When there are multiple pesticide applied areas, the same gradient pattern is used as previously described , but samples are obtained in two directions toward the treated areas.

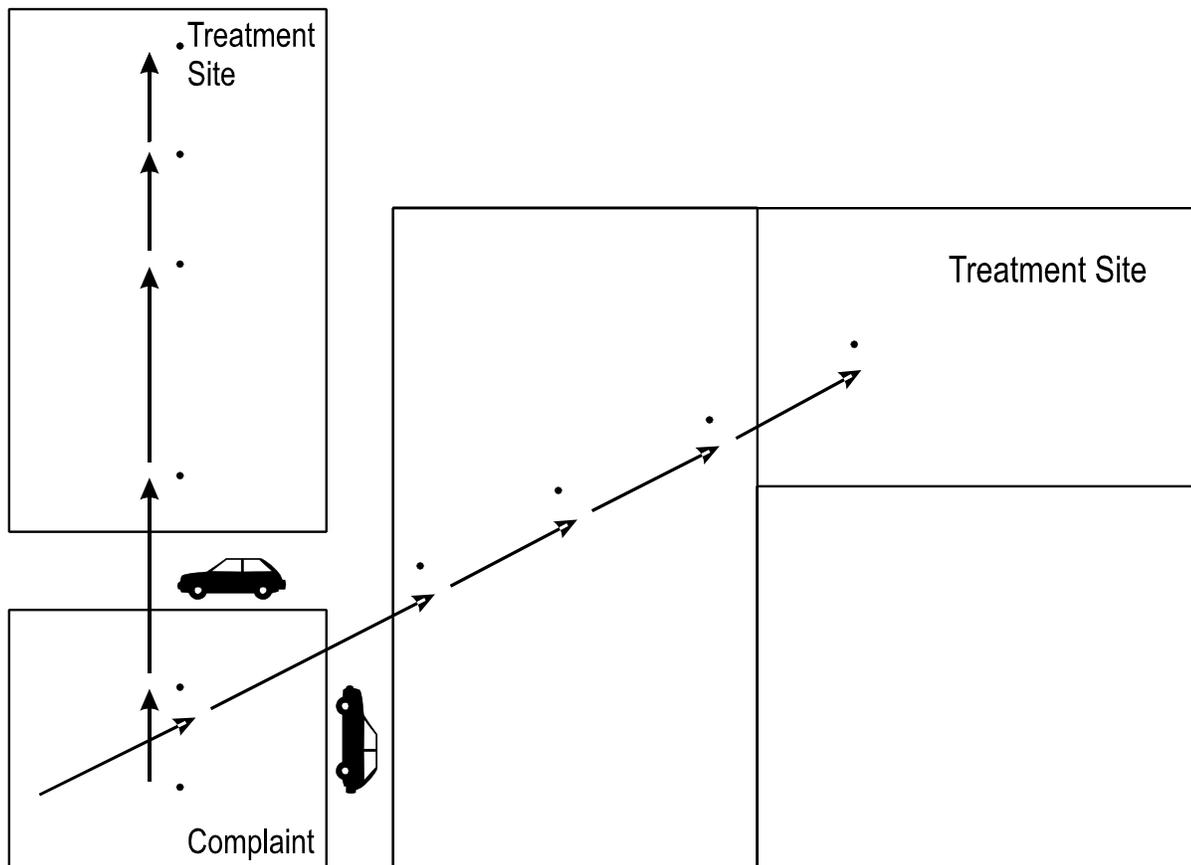


Figure 13-4: Gradient Sampling Diagram -Property Loss Incident

Agricultural Pesticide Misuse

Sample Collection

- < Vegetation/soil samples in gradient pattern
- < Commodity, if harvesting
- < Wipes from vehicle
- < Clothing

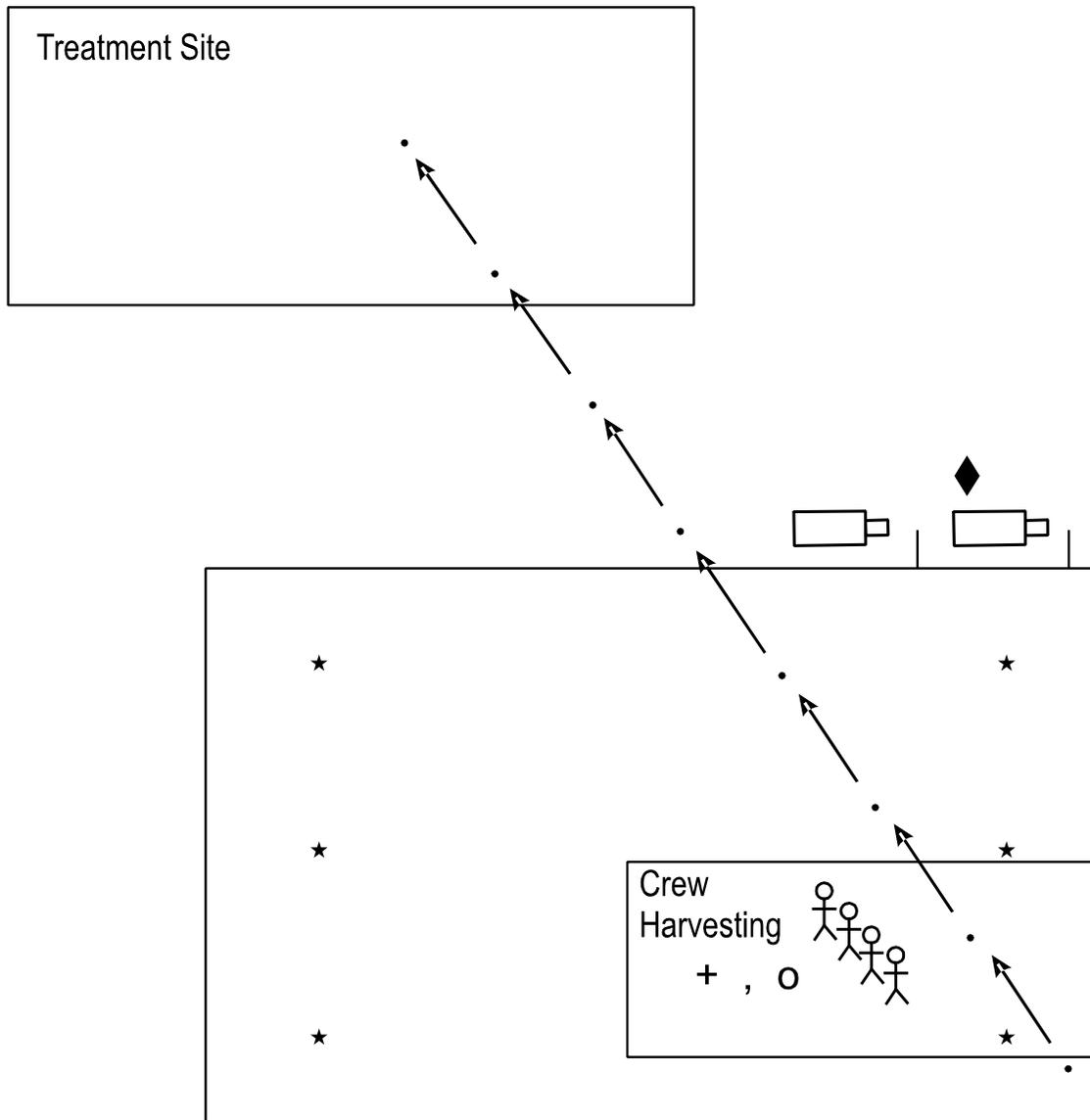


Figure 13-5 - Gradient Sampling Diagram - Agricultural Pesticide Misuse

**Structural Pesticide Misuse**

NOTE: Labeling allows a 5 foot band around perimeter of house and 2 to 3 foot up the foundation wall.

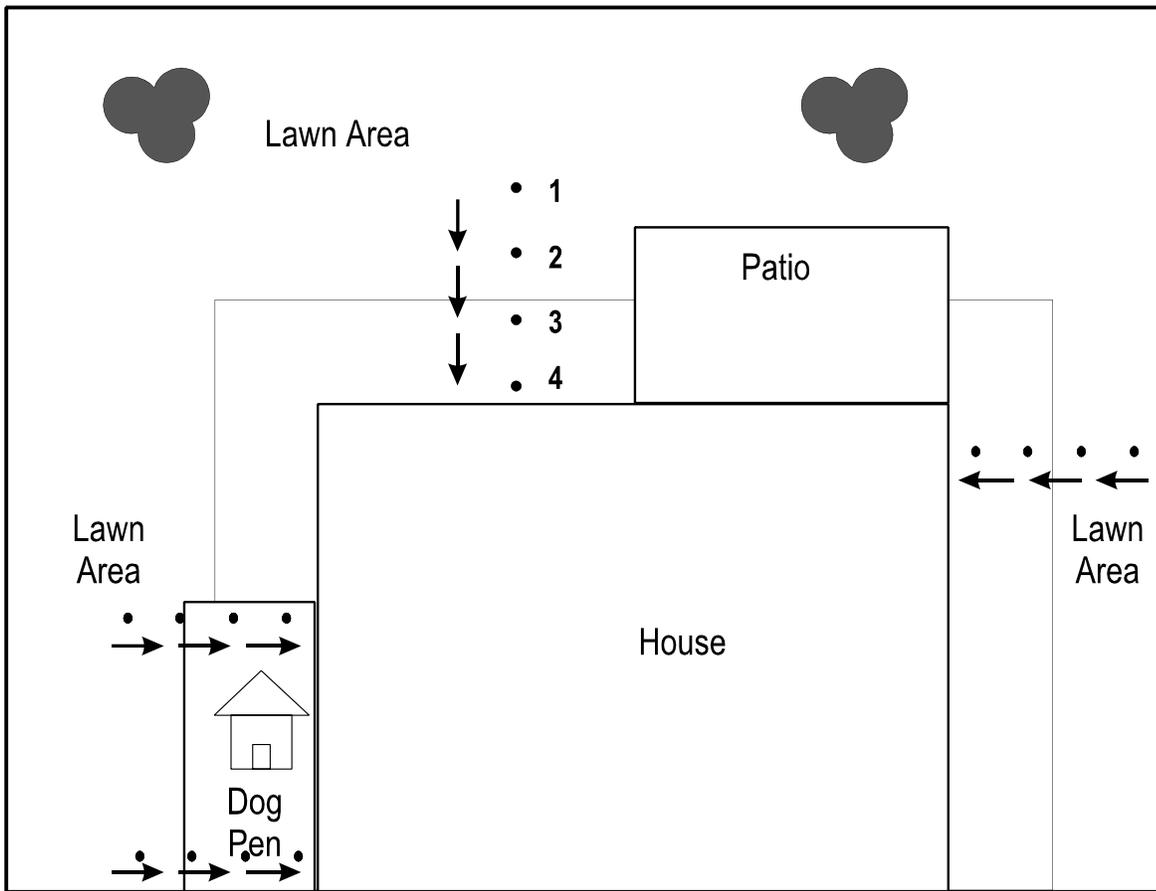


Figure 13-6: Gradient Sampling Diagram - Structural Pesticide Misuse

**Discrete Soil Sampling (Known Depth)**

Soil samples at a known depth are collected when the pesticide is suspected of being incorporated, band treated, shanked, or moved below the soil surface (leaching). If the samples are not collected at the proper depth, the sample results will be misleading. This type of sampling may be collected in a grid pattern within a field or site.

After taking a control sample, select a specific sample location and measure an area of approximately one-square foot. Record the measured sample area in the investigative notes.

If it is suspected that chemical leaching has occurred at the sample site, dig a sampling hole and collect soil from various depths (e.g., 3-6 inches, 6-9 inches, etc.). After digging the hole, decontaminate the sampling instrument and shear away the soil face at the depth desired starting with the deepest sample. Decontaminate the sampling instrument or use a clean jar and collect the sample.

Repeat this procedure moving upward in the sample hole until all samples are collected. If a soil probe is available, remove the soil to the beginning depth to sample. Take several core samples to the desired depth using the probe. NOTE: It is not recommended to use the probe when a band or side-dress treatment was used. Since it is difficult to determine where the band treatment is located the probe technique could miss the pesticide and give misleading results.

Samples must be recorded and handled the same as described above

### Soil Sampling In Furrowed Fields

**Single row beds:** combine soil from the imaginary area outlined in the figure below in a container and fill a 1 quart jar.

**Double row beds:** Center furrow to center bed.

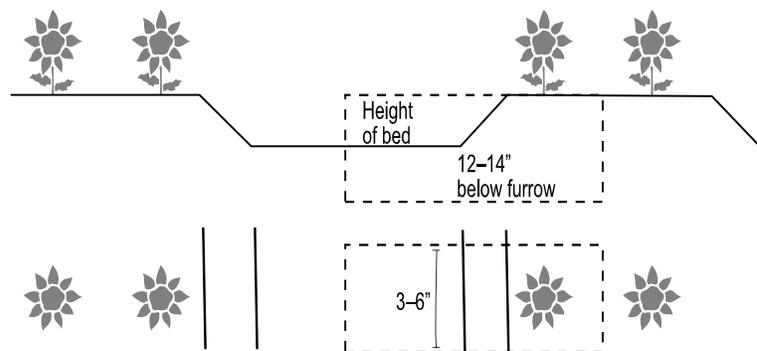


Figure 13-7: Soil Sampling in Furrowed Fields

### **Discrete Soil Sampling (Known Depth, Furrowed Field)**

Chemicals may have been applied in bands or side-dressed in furrowed fields. In order to sample from the appropriate area, a shovel is needed to cut across sections perpendicular to the direction of furrow at each sample site.

#### Single Rows

After taking a control sample, start at the center of the furrow and sample across the bed to the center of the opposite furrow. Collect soil from an area 3"-6" wide and 12"-14" deep as measured from the top of the bed.

#### Double Rows

If the field is laid out in double row beds, sample from center of furrow to center of bed at 3"-6" width and 12"-14" depth.

Mark the location of the sample area on the diagram indicating distances from each sample, depth and width of sample, landmarks, and field borders.

## Grid Pattern Soil Sampling

Grid pattern soil sampling is used to establish the pattern of contamination of the incident site. The sampling pattern must represent the entire field or site. Each point on the grid pattern represents a sample and must be kept separate from the others. There are several pesticides (e.g. DCPA and chlorothalonil) that are long lasting in the environment and adhere to soil particles. Cultural practices (i.e., disking) and wind can move these particles from adjacent fields to a crop, creating a potential residue problem. The grid pattern sampling results can be used to document the transport of the soil particles. If misapplication to part of a field is suspected, but the treated area is unknown, the grid sampling pattern must be used to define the affected area.

Collect soil samples at the appropriate depth in a grid pattern following the procedures indicated for a discrete soil sample (surface, known depth, furrowed field). Each sample will represent one point on the grid for that field or site. Do not composite these samples.

After taking the control sample, the sampling grid pattern must start approximately 100 feet from the edge of the field, depending on the field size. As a rule of thumb, the closest sample distance from the edges must represent 10 percent of the width and length of the field or site. Each sample must be in line with, and at an equal distance apart from, the other samples in the grid pattern. Record the sample locations in the investigative notes.

If the field or site is suspected of being only partially contaminated (i.e., three-quarters of the site was treated), collect samples from the area of lowest concentration to the highest.

## Gradient Soil Sampling

Gradient soil sampling is usually conducted to prove drift from a treated area. If drift is suspected to have occurred to a field and the pesticide can be detected in soil, then gradient sampling may be of use. A gradient pattern may also be used to determine if a structural or residential application was made according to label directions.

Samples must be collected from defined areas in the field or site similar to the methods indicated in the procedures for a discrete surface soil sample as described in Figure 13-7.

Collect surface soil samples in a gradient pattern at an equal distance apart with at least one control sample (collect first) outside the contaminated area and one or more samples from the suspected source area of contamination.

Always sample from an area of suspected lowest concentration in a direction towards the area of highest concentration (treatment site). Collect gradient samples towards each suspected source if more than one source of contamination is suspected.

## Composite Soil Sampling

Composite soil samples are taken to determine if an area is contaminated or to determine if other samples must be analyzed. The composite sample is made up of several sub-samples that are combined to represent a field or site.

If composite samples are desired, combine soil from the grid point samples to make a composite sample. Collect enough soil for each grid point sample to allow for the requested analyses.

## Discrete Sediment Sampling

If equipment is not available to collect a sediment sample or assistance is needed, contact the supervisor. The supervisor will make the arrangements to have the appropriate agency assist or collect the samples.

Pesticide residues can accumulate in the bottom sediment of lakes and streams. It may be necessary to conduct sediment sampling to document the pesticide source. There are commercially available devices for sediment sampling, but these devices often require extensive cleaning between sampling to prevent cross-contamination. Directly scooping sediment into a glass jar is recommended for shallow sampling situations.

Sediment contents can be flushed or diluted as the jar is lowered or retrieved through water exceeding a few inches in depth. Therefore, a disposable core tube is recommended for unconsolidated sediment and use of a commercial sediment-collection device is recommended for firm bottom deposits.

Carefully lower disposable core tube or other sampling device through water into sediment (minimize disturbing the sediment).

Retrieve approximately one quart of sediment.

Transfer sediment directly into a clean glass sample jar or a clean pan. Remove rocks, leaves, and other debris from sediment before transferring to the wide mouth glass jar. Seal with Teflon or foil-lined lid.

Mark the location of the sample area on the diagram indicating distances from each sample, landmarks, and field borders.

Dispose of or clean sampling tools. Rinse pan, if used, with isopropyl alcohol and flush with clean water before collecting additional sediment samples.

## Water

The following guidelines are for collecting samples of surface water and are designed to detect pesticide residues in surface water such as lakes, streams or ponds resulting from some type of misuse (i.e., off-site drift, overspray) of the pesticide. If pesticide contamination of groundwater is suspected, contact the supervisor to determine the appropriate federal, State, or local agency for follow-up.

A determination should be made whether or not to wear shoulder-length gloves and chest-high waders whenever contact is made with potentially contaminated water.

### ***Discrete Surface Water Sampling***

Use two (2) clean one-liter amber glass containers with an aluminum foil or Teflon seals under screw cap. Fill bottles to top leaving no air space for pesticides to volatilize. Make sure samples do not freeze [if amber glass containers are not available use two (2) one-quart large mouth jars and wrap each bottle with aluminum foil to exclude light].

Sample as close as possible to the apparent source of contamination.

Avoid sampling sediment that is disturbed by your movement. Wear shoulder-length gloves and chest-high waders if dermal exposure may be a problem.

If the suspected pesticide is water soluble, the sample must be drawn from a lower depth. If the pesticide is oil-based, or oil is a part of the tank mix and the alleged misapplication was made across the water surface, then the sample can be drawn from the surface layer.

Lower the glass bottle to the desired depth with the cap on. Remove the cap under water, and allow bottle to fill. Replace the foil-lined (or Teflon lined) cap and lift the bottle out of the water. For surface samples dip the bottle into the water surface and allow it to fill. Jars must be filled completely to the rim, with no head space and with the jar lid rubber seal down.

Several samples distributed around ponds or lakes are preferable to only one sample. If only one sample is taken, draw several sub-samples from different locations around the body of water and combine as a composite into two (2) clean one-liter/quart containers.

If the water is too shallow to immerse a jar, use another clean jar to fill the sample jar.

Mark the location of the sample area on the diagram indicating distances from each sample, landmarks and field borders.

Samples must be chilled or refrigerated and shipped as soon as possible. **DO NOT ALLOW SAMPLES TO FREEZE.** An ice chest with regular or "Blue-Ice" can be carried into the field for this purpose.

### **Air**

Generally, volume air sampling is conducted by the EPA laboratory staff or Environmental Services Division (ESD) in concert with the inspector. Since they have the unique equipment, chemicals, knowledge, and experience needed to operate air sampling equipment, it is recommended that they be contacted if volume air

sampling is essential. The pesticide inspector will retain the lead for the investigation and other personnel will assist.

Basically, there are two types of air samplers used. High Volume (Hi-Vol) samplers used to measure low concentrations of pesticides over long periods of time, and Low Volume (Lo-Vol) samplers used to measure high concentrations of pesticides over shorter periods of time. These are not hard, fast rules, and conditions often dictate which sampler is best.

Both Hi-Vol and Lo-Vol samplers draw air through glass cylinders containing a medium designed to trap the pesticides of interest.

### **Air Sampling Indoors**

Either Hi-Vol or Lo-Vol samplers can be used depending on expected concentrations. NOTE: Air samplers produce a moderate noise. They should be positioned where they will not unnecessarily disturb other persons in the structure, if possible.

Hi-Vol samplers must be vented out of the dwelling to ensure that air will not be recycled through the machine.

Rooms with cigarette smoke or gas appliances must be avoided; any gases or suspended smoke particles in the area will contaminate the sample.

### **Air Sampling Outdoors**

Either Hi-Vol or Lo-Vol samplers can be used outdoors.

Sampling equipment must be positioned to avoid exposure to engine exhausts, running motors, cigarette smoke, or any other non-target air contaminants.

Sampling equipment must also be protected from rain and direct sprays from application machinery. Shelter hoods are used to protect the equipment in such situations.

Use proper sample preparation and Sample Collection Recording. Air samples must be sealed and delivered directly to the lab.

## **Pesticide Formulations (Technical Grade)**

Sampling pesticide formulations for investigative purposes may be necessary to provide evidence of pesticide misuse, misformulation, product composition, cross-contamination or other problems. In order for the analytical results of these samples to substantiate a finding that a violation exists, the samples must be representative of the total amount of the material sampled.

Each sampling situation in an investigation/inspection must be judged separately as to number, type, and method. The following general guidelines must be observed:

- < Read and follow all precautionary statements on the label before sampling a formulated pesticide material (i.e., protective clothing and equipment requirements). If a label is

not available, wear the maximum safety equipment (i.e., respirator, Tyvek suit, coveralls, rubber gloves, rubber boots, and goggles).

- < Wash thoroughly with soap and water before eating, drinking, smoking or using the bathroom.
- < If possible/practical, collect the entire container with its contents. Smaller samples can always be collected from the larger container at a later date.
- < Since not every ounce of formulated pesticide material can be sampled (e.g., bulk containers) and analyzed, design sampling so all portions of the pesticide are “represented” in the final sample.
- < Sample tools must be cleaned with hexane or alcohol and rinsed with clean water or disposed of properly before collecting additional samples.
- < Avoid cross-contaminating samples by keeping these samples separate from all other samples (i.e., residue) at all times. The following guidelines must be used to avoid cross-contamination:
  - Liquid bulk samples are to be collected in 8 oz. amber glass bottles with Teflon lined caps unless otherwise stated on the label.
  - Dry bulk samples are to be collected in glass pint or quart jars, or pint metal type paint containers.
  - Small retail packages can be collected as a sample. Four to eight ounces of product is sufficient sample size.
- < Use proper sample preparation and sample collection recording. Review label for storage. Cool sample, unless otherwise stated on the label. **DO NOT ALLOW TO FREEZE.**
- < Unless certified sterile containers are used, wash/rinse the container and lid with hexane or alcohol and allow to air dry prior to collecting the sample. Note this in the Sample Collection Report.

### **Tank Mix**

Laboratory analysis of tank mix samples will identify the active ingredient and any possible contaminants in the tank mixture. Analysis results can be reported as either percentage by weight or parts per million.

It is the responsibility of investigators to protect themselves and others during pesticide handling and sampling activities. Tank mixes may be highly toxic. Protective clothing and safety equipment must be used by investigators when sampling. Refer to pesticide labels for precautionary statements. Rubber/Neoprene

gloves and goggles/face shield must be worn when sampling all tank mixes. Wear a respirator if required by the label to protect against vapors, dusts, or powders. If the tank mix ingredients are unknown, assume they are the most hazardous and wear all required safety equipment. Be careful when working around machinery and at busy mixing/loading sites. Be aware of hoses and fittings that may be under pressure or leak.

End use dilutions must be collected in glass 8 oz. or 16 oz. bottles. Always use glass bottles or jars with Teflon lined caps (lids) or hexane-washed foil-lined lids. Do not allow tank mix solutions to contact rubber or plastic as these materials may affect the analytical results. Do not use foil-lined lids if the pesticide reacts with metal. Thoroughly agitate liquid in service container or tank.

Use a sterile or washed siphon tube and collect a composite sample from three depths near tank bottom, middle, and near the top of the liquid level. If the solution is adequately mixed to ensure uniformity, a sample can be collected from the drain system. Collect a composite sample from as many points in the drain system as are available. Application rigs can be sampled at spray boom nozzles. Following actual application, have the operator loosen boom nozzle and drain the pesticide mix into a glass sample container. Be sure that the operator tightens the nozzles on the boom after the sample has been taken.

To reduce the possibility of spillage, do not fill the sample jar or bottle above the bottom of the thread line. If the pesticide is highly volatile, fill to the top of the jar to prevent volatilization into the air space.

Use proper sample preparation and Sample Collection Recording. **DO NOT ALLOW TO FREEZE.**

Decontaminate all tools and change or wash gloves to prevent cross-contamination of samples. Do not store or ship tank mix samples with or near foliage or soil samples.

After collecting the samples wash thoroughly with soap and water before eating, drinking, smoking or using the rest room.

For specific sampling procedures for a particular sampling situation, investigators should discuss with the supervisor or laboratory personnel the protocol that is appropriate for the particular situation at hand.

### **Animals, Fish, Honeybee Sampling**

Dead animals, fish, and honeybees must be sampled fresh before decomposition, if possible.

Use disposable gloves when handling animal samples because of the possibility of disease transmission.

Small animals and fish must be placed in a heavy, inverted polyethylene bag, properly identified, and frozen as soon as possible. At least 500 grams is needed per sample.

Collect a minimum of four ounces of fresh dead bees or honey and a minimum of one ounce of pollen. Remember to collect enough for each analysis requested. Place sample in a clean, unused jar.

Use proper sample preparation and sample collection recording.

Chill all animal, fish, and bee samples as they are collected to prevent further degradation. If decomposition is evident, upon collection indicate so on the Sample Collection Record.

Freeze and ship all tissue samples as quickly as possible. Maintain a Chain of Custody.

### Surface (Wipe) Sampling

Surface or wipe sampling is conducted to establish the presence of a pesticide on a surface.

#### Discrete Surface Sampling

Equipment needed:

- < Disposable latex gloves
- < Solvent (isopropyl alcohol or hexane)
- < Sterile pad
- < Disposable paper template
- < Permanent marker
- < Large polyethylene bag

Discrete surface sampling include the following steps:

- < **Collect Control Sample.** Before entering the area to be sampled take a control sample. While wearing disposable gloves, pour the solvent over the sterile pad. **Do not contaminate the solvent by placing the pad over the mouth of the solvent bottle.** The control sample must be prepared and identified following the procedures outlined below.
- < **Select Target Site.** When possible select a site showing visible residue. Try to avoid areas known to contain waxes because they may interfere with the analysis. Smooth “inert” surfaces are the preferred area to collect the sample (i.e., windshield, etc.). Sampling uneven surfaces (such as rugs, furniture, walls, walkways, counters), however, is also possible.
- < **Prepare Sample Site.** While wearing disposable gloves, tape a template to sample surface. The template will delineate the sample area at the target site. **A new template and gloves**

**must be used for each sample location.** If a template cannot be placed on target site, delineate the sample area using masking tape of approximately 100 square centimeters in area. Photograph the area as necessary.

- < **Collect Wipe Sample.** Surface areas are sampled using a sterile cotton pads (2" x 3") or filter paper discs moistened with solvent. While wearing disposable gloves, pour isopropanol or hexane over the foam pad and moisten it completely. Shake off excess solvent. **Do not contaminate the solvent by placing the foam pad over the mouth of the solvent bottle.** The target area of the template is to be completely wiped, with circular motions and back-and-forth motions, with the first side of the wipe swabbed in a consistent direction 90 degrees to the first swabbing. Depending on the surface conditions, wipes may also have to be taken by dabbing the surface area within the template.
- < **Prepare Sample.** Place the sampling pad in the jar, can, or other appropriate sample container. Using a permanent marker, identify the sample collection number, date, and inspector's initials on the sample container. Place each sample collected in a large polyethylene bag and follow the procedures outlined. To document the area sampled, take a photograph of the sample area to include: the area wiped, the sealed sample container, and the template still in place.
- < **Prepare Collection Record.** Record the surface area type and sample location on the Sample Collection Record, on the incident diagram, and in the investigative notes. Other information recorded on the Sample Collection Record. Form includes the following: the solvent used, the suspected ingredients in the pesticide spray solution, and whether the surface sample represents pesticides in concentrate, tank mix, or residue from drift or overspray.
- < **Sample storage and shipment.** Store the samples in the freezer or refrigerator and ship on dry ice. Pack the Sample Collection Record and samples in the same manner as the soil/foilage samples.

#### ***Grid Pattern Surface Sampling***

Grid pattern samples are taken to establish uniform or partial contamination of the incident site. They can be used to delineate a contaminated site (treatment site) from non-treated sites. For example, it may need to be proven that a broadcast carpet treatment occurred when labeling only allowed a baseboard treatment.

Collect samples in a grid pattern following the procedures indicated for a discrete surface sample, as described above. Each sample represents one point on the grid for that site. Do not composite the

samples. Always collect a solvent control sample prior to any other sampling.

If the site is suspected of being partially contaminated, start sample collection in the area of least contamination.

If multiple analyses will be requested, collect companion samples.

Surface samples must be collected from similar surface areas. Identify on the diagram the location and area from which each sample was taken, with distances from landmarks, walls, and between samples clearly indicated.

Use proper sample preparation and Sample Collection Recording.

### **Gradient Surface Sampling**

Gradient surface samples are taken to establish a drift pattern in or on a structure. Always sample from an area of lowest concentration in a direction towards the area of highest concentration (treatment site) to prevent contamination of samples.

Samples must be collected from defined areas at the site similar to methods indicated in the procedures for a discrete surface sample. Always collect a solvent control sample prior to any other sampling.

Collect samples in a pattern at an equal distance apart with at least one sample outside of the contaminated area (if possible) and one or more samples from the suspected source area of contamination. The gradient pattern must be in a straight line.

If multiple analyses will be requested, collect companion samples for a discrete surface sample.

Collect samples from similar surface areas. Identify the location on the diagram and the area from which each sample was taken. Include distances from landmarks, walls, and between samples.

Use proper sample preparation & Sample Collection Recording.

### **Clothing**

Be selective when collecting clothing samples. Collect clothing only from people who were allegedly contaminated. Consideration must be given to the type of incident involved. Garments, such as shoes (footwear), could be collected if an applicator was allegedly exposed to a pesticide because of failure to wear protective equipment. Shirts, scarves, or jackets could be collected if they were exposed to pesticide drift.

Clothing samples are usually collected away from the incident site. Should the history of the clothing be unknown, attempt to find out more about the integrity of the sample. Ask the people involved if the clothing has been washed since the incident. If the clothing has been washed, the investigator must not collect the sample unless there are special circumstances which dictate sampling. Consult with the supervisor for guidance if unsure.

Inform those people involved that the clothing will not be returned.

Wrap each article in aluminum foil prior to placing it into the poly-bag.

Place each sample in a separate large, inverted 12" x 30" heavy polyethylene bag. Properly knot and seal each bag. Identify and officially seal samples immediately as they are taken.

Use proper sample preparation & Sample Collection Recording.

When submitting clothing samples for analyses, consideration must be given to the type of incident involved. Clothing samples are collected to determine if pesticide residues are present. They are not used to determine whether the exposure resulted in a health hazard. If the affected area of the clothing is known (i.e., spot caused by spill), the investigator could cut the affected area out and submit it to the laboratory. In some situations it might be better to submit the entire garment. Indicate on the Sample Collection Record the area of the clothing the Laboratory should analyze (i.e., shoulder, sleeve, front, etc.).

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## SAMPLE STORAGE, PRESERVATION, AND SHIPPING

The proper collection, storage and shipping of samples are all critical elements of the sampling process and can affect the analysis results. Steps must be taken early in the sampling process to avoid anything that could compromise the integrity of the sample, such as loss, contamination or tampering.

Ideally, samples should be analyzed as soon as possible after they are collected. In many situations, however, this may not be possible and consideration must then be given to assuring the integrity of the sample by utilizing proper storage, preservation, and shipping methods.

### Storage and Preservation

If samples must be stored temporarily, it is best to refrigerate or even freeze them to prevent deterioration of the sample and degradation of the chemical. Contact the supervisor or laboratory if in doubt about the specific requirements for storage of a particular kind of sample.

All samples should be stored in an insulated cooler to protect from extreme heat and cold during the transit to the laboratory from the time of collection. In extreme hot conditions, it may be necessary to include ice inside the cooler in order to maintain the integrity of the sample. The inspector should read and follow the label statement for storing the samples under or over the listed temperatures.

Table 13-1 summarizes the general requirements for preserving various sample types during storage (i.e., field and laboratory) and shipping to the laboratory. Refer to the specific sample type in the “Sampling Procedures” section of Chapter 9 in this manual for additional information.

***Table 13-1: Sample Preservation***

Sample Type	Container	Field	Storage	Ship
<b><i>Foliage</i></b>				
Discrete	PB	C	F	DI
Grid	PB	C	F	DI
Gradient	PB	C	F	DI
Composite	PB	C	F	DI
Dislodgeable	GJ	C	R	WI
Commodity (field, packed)	PB	C	R	WI
<b><i>Soil</i></b>				
Discrete (surface)	GJ	C	F	DI
Discrete (known depth)	GJ	C	F	DI
Discrete (furrowed field)	GJ	C	F	DI
Grid	GJ	C	F	DI
Gradient	GJ	C	F	DI
Composite	GJ	C	F	DI
<b><i>Sediment</i></b>	GJ	C	F	DI
<b><i>Water</i></b>	GJ	WI	R	WI
<b><i>Air</i></b>	GJ	DI	F	DI
<b><i>Animals, fish, honeybees</i></b>	GJ	C	F	DI
<b><i>Surface</i></b>				
Wipe	GJ	C	F	DI
Grid	GJ	C	F	DI
Gradient	GJ	C	F	DI
<b><i>Clothing</i></b>	PB	C	F	DI
<b><i>Tank-Mix</i></b>	GJ	C	R	WI

**NOTE:** All sample containers are to be sealed in a plastic bag in the field.

(C) — Chill (Wet Ice or "Blue-Ice")

(DI) — Dry Ice

(F) — Freeze

(GJ) — Glass Jar/sealed in Plastic Bag

(R) — Refrigerate

(PB) — Sealed in Plastic Bag

(WI) — Wet Ice

## Shipping Procedures

Packaging and shipping samples must be done properly, using care to ensure that they remain intact when they arrive at the laboratory. Pesticide formulation samples must be packaged to avoid spillage, leakage or deterioration and the possibility of endangering the safety of persons or the environment. Ship samples in accordance with Department of Transportation (DOT) regulations. Maintain the Chain of Custody.

The following are general guidelines to be observed when packaging samples for shipping:

- < Determine if the sample is considered hazardous material under U.S. DOT regulations, (49 CFR Part 172.101) as these materials require special packaging, labeling, and UPS procedures. In most cases, UPS will be utilized for sample shipment to the lab. Do not send samples through the Parcel Post. Most of the samples that are collected are NOT considered hazardous materials.
- < Investigative samples must be shipped to the laboratory as soon as possible, but must not be shipped on Friday unless special laboratory arrangements are made, since the samples would not be delivered to the laboratory until the following Monday. Samples held over the weekend must be kept under dry ice, chemical ice, or contained wet ice. Routine samples must be shipped weekly, on any day of the week.
- < Samples to be analyzed for pesticide residues (foliage, soil, water, animal etc.) Require that a temperature be maintained during shipping that will prevent deterioration. Refer to the Sample Preservation Table.
- < Samples must be carefully packed in coolers and sealed with fiber reinforced tape to avoid breakage in transit. Samples should be packed with plenty of crumpled newspapers or similar material. If there are several samples, do not ship both liquid and dry samples in the same cooler, if at all possible.
- < Under no circumstances should pesticide samples be shipped in the same carton with samples of feed, fertilizer, or seed.
- < UPS will not ship any single carton weighing over seventy (70) pounds.
- < Place properly bagged and labeled samples in shipping container and immobilize samples with suitable packing material such as crumpled newspaper or styrofoam. Seal the shipping container.

- < Pack liquid samples in sufficient absorbent material to absorb and retain any leakage that might occur. It may be necessary to “over pack” the sample.
- < Clearly mark shipping container with handling instructions, such as “Handle With Care,” “Glass,” “This Side Up,” or other appropriate wording.
- < Comply with all applicable packaging and shipping requirements of DOT.
- < Ship or deliver the samples to the appropriate location as soon as possible and maintain Chain of Custody.
- < No special markings or diamond DOT labels are required on the package, unless the product samples are classified as hazardous.

#### ***Hazardous Materials Shipments - UPS & FEDEX Procedures***

The above procedures are not sufficient to ship samples of products classified by DOT as hazardous. Hazardous classifications are generally based on three independent elements:

- < Toxicity. Shipment of any pesticide formulation sample which bears a label containing the signal words “DANGER - POISON”. These products may be sampled as “Documentary Samples”, or upon request from the office, will be collected and hand delivered to the lab. These products have an LD<sub>50</sub> of 50 milligrams/kilogram and are considered as Class A or Class B poisons. UPS will not ship pesticides which are in the “POISON” hazard class without very special packaging.
- < Flammability. Any pesticide product with a flash point below 100° F. is considered a hazardous material. Look for “Flammable” DOT diamond stickers on the container or shipping carton of the product or for statements on the label such as: “Do not use near heat or open flame.” Limited amounts of flammable products may be shipped by UPS.
- < Corrosiveness. Corrosive substances are those which cause irreversible skin damage. The label on these products will read “Corrosive-causes eye and skin damage”. Most bowl cleaner - sanitizer products will be in this class. Most of these can be shipped in the same manner as flammable liquids.

**IF AT ANY TIME  
THERE IS A QUESTION  
REGARDING PROPER  
SHIPPING  
PROCEDURES FOR A  
PRODUCT, PLEASE  
CALL YOUR  
SUPERVISOR.**

Except in rare circumstances, the only hazardous materials that will be encountered are some of the pesticide formulations that have been sampled. Residue and pesticide impregnated fertilizer samples normally fall outside of the “hazardous” definition because of the low concentrations of pesticide active ingredient actually present. All samples must be shipped via UPS or FEDEX, motor freight, or transported by the inspector, and NEVER U.S. mail.

### **Investigator's Shipment Procedures**

The following procedures should assist the investigator in shipping samples via UPS or Federal Express (FedEx) in compliance with applicable regulations.

Look for DOT diamond labels indicating "POISON," "FLAMMABLE," or "CORROSIVE" on the product container, or shipping carton. Again, do not collect or ship any pesticide bearing the signal word "POISON."

### **UPS Shipments**

Look for the name of the pesticide or the pesticide active ingredient under the list entitled "Hazardous Materials Shipping Names - UPS." If the chemical name is found under this list, the investigator will need to take the following actions:

- < Complete a UPS five part UPS Hazardous Material Form (U1114), a Shipper Certification Form (U1208), and a standard UPS shipping form (U1203) (call 1-800-742-5877 to order these forms directly from UPS).
- < In order to comply with Department of Transportation regulations (49 CFR 177.817) UPS shippers of Hazardous Materials must prepare a UPS Hazardous Materials Form (Form U1114) for each parcel requiring documentation. All entries must be legible and printed manually or mechanically in English. Affix form to the parcel, next to the address label. (Note: UPS Hazardous Materials Form does not replace or supersede other labels or marking required by the DOT). Remember that ORM items do not require a 5 part form (U1114) or UPS shipper certification (U1208), unless they meet the definition of a hazardous substance.
- < Form U1208 must state the complete and correct DOT shipping name, hazard class, identification number, and DOT label required as specified under the shipment name list. Also state the amount of material actually being shipped. Do not ship any other samples with any sample considered hazardous. Write the shipping name of the chemical on the outside of the shipping carton.

If the pesticide is not on the list, but there is a diamond sticker, select the appropriate shipping name for the following choices:

- < Compound, weed killing liquid (flammable or corrosive) FLAMMABLE LIQUID NA1993 or CORROSIVE MATERIAL NA1760.
- < Compound, weed killing solid (oxidizer). OXIDIZER AN1479.
- < Disinfectant, liquid (corrosive). CORROSIVE MATERIAL UN1903.

- < Insecticide, liquid, N.O.S. (flammable) FLAMMABLE  
LIQUID NA1993

UPS packages must be shipped using the following methods:

- < Packages can be dropped off at UPS customer counters. Since the counters are open only at certain times during the day, determine the hours of service of the counters for most efficient use.
- < For an additional charge, UPS will pick up a package at any location. Use the following procedures for package pick-up:
- < Samples must be packed and labeled as indicated above. It will be necessary to weigh or estimate the weight of the package.
- < Phone UPS at 800-242-2111 the day before the carton is to be picked up. UPS will visit the same pick-up point each day for the remainder of the week for the one time per week charge, if desired. Initially, an appointment will need to be made with a UPS representative to establish a UPS shipper number.
- < If the samples are classified as hazardous materials, complete a five part UPS hazardous material form (U1114) and attach it to the carton. See Table 13-2 for a list of UPS hazardous materials shipping names.
- < For any shipment, also complete a UPS form U1203. After initial establishment of the shipment number, UPS shipping costs will be billed directly to your account. Retain copies of the shipping forms for future shipping documentation.

**Table 13-2 - Hazardous Materials Shipping Names - United Parcel Service**

Product — Proper Shipping Name (DOT Label Reg.) Hazard Class — ID. No. Special Instructions			
#1	<b>Allethrin</b> (none) ORM-A-NA2902 Package Marking Only	#2	<b>Aluminum Phosphide</b> FLAMMABLE SOLID UN1397
#3	<b>Azinophos Methyl Mixture Liquid</b> POISON B NA2783 DO NOT SHIP	#4	<b>Bipyridilium Pesticide Liquid N.O.S.</b> POISON B NA2783 DO NOT SHIP
#5	<b>Cadmium Sulfate N.O.S.</b> (none) ORM-A NA1693 Package Marking Only	#6	<b>Carbamate Pesticide Solid N.O.S.</b> (none) ORN-A NA2757
#7	<b>Carbamate Pesticide Liquid N.O.S.</b> FLAMMABLE LIQUID UN2757	#8	<b>Carbaryl</b> (none) ORM-A 2757 Package Marking Only
#9	<b>Carbofuran</b> POISON B NA2757 DO NOT SHIP	#10	<b>Carbon Tetrachloride</b> ORM-A NA1693 (none) Package Marking Only
#11	<b>Diazonin</b> (none if less than 1 lb.) Package Marking Only	#12	<b>2,4-Dichlorophenoxy-acetic</b> (none) ORM-A NA2765 Package Marking Only
#13	<b>Dichloropropene &amp; Propylene</b> Dichloride Mixture FLAMMABLE LIQUID NA2047	#14	<b>Dinoseb</b> — See #29
#15	<b>Disulfoton Mixture Dry N.O.S.</b> POISON B NA2761 DO NOT SHIP	#16	<b>Endosulfan Mixture Liquid N.O.S.</b> POISON B NA2761 DO NOT SHIP
#17	<b>Ethylene Dibromide</b> (none) ORM-A UN1605 Package Marking Only	#18	<b>Ethylene Dichloride</b> FLAMMABLE LIQUID UN1184
#19	<b>Ethylene Oxide</b> UN1040 FLAMMABLE LIQUID	#20	<b>Formaldehyde Solution</b> (Flammable or none) ORM-A UN1198 Package Marking Only

Product — Proper Shipping Name (DOT Label Reg.) Hazard Class — ID. No. Special Instructions			
#21	<b>Hypochlorite Solution</b> (Corrosive if over 7%) CORROSIVE UN1791 or ORM-B NA1791 If ORM-B, Package Marking Only	#22	<b>Lindane (none)</b> ORM-A NA2761 If under 1 lb. Package Marking Only
#23	<b>Malathion (none)</b> ORM-A Package Marking Only	#24	<b>RQ Methoxychlor</b> (if over 1 lb.) ORM-E NA2761
#25	<b>Naphthalene (none)</b> ORM-A UN1334 Package Marking Only	#26	<b>Paraquat (Gromoxone)</b> See #4
#27	<b>Propionic Acid</b> UN1848 CORROSIVE MATERIAL	#28	<b>Sodium Chlorate</b> OXIDIZER UN1495
#29	<b>Substituted Nitrophenol Liquid N.O.S.</b> Flammable or Poison B FLAMMABLE LIQUID UN2780 DO NOT SHIP IF POISON B	#30	<b>Thiram (none)</b> ORM-A NA2771 Package Marking Only
#31	<b>Toxaphene (none)</b> ORM-A NA2761 Package Marking Only	#32	<b>Triazine Pesticide Liquid N.O.S.</b> FLAMMABLE LIQUID UN2764
#33	<b>Zinc Chloride Solution</b> CORROSIVE MATERIAL UN1840	#34	<b>Zinc Phosphide</b> POISON B UN1714 DO NOT SHIP

### FedEx Shipments

The package must meet all applicable DOT packaging, marking, and labeling requirements before it can be shipped by FedEx. See Table 13-3 for packaging, marking, and labeling requirements.

Complete the FedEx Dangerous Good Airbill (Exhibit 13-1) (call 1-800-463-3339 to order these forms directly from FedEx). See Table 13-4 for instructions on how to complete the FedEx Dangerous Goods Airbill. If you need further help completing this form, call 1-800-463-3339, ext 922-1666 for assistance.

To determine the proper shipping name, use the UPS hazardous materials shipping name (see Table 13-2) or, if there is a diamond sticker on the container, select the appropriate shipping name from the following choices:

- < Compound, weed killing liquid (flammable or corrosive) FLAMMABLE LIQUID NA1993 or CORROSIVE MATERIAL NA1760.
- < Compound, weed killing solid (oxidizer). OXIDIZER AN1479.
- < Disinfectant, liquid (corrosive). CORROSIVE MATERIAL UN1903.
- < Insecticide, liquid, N.O.S. (flammable) FLAMMABLE LIQUID NA1993.

Packages can be dropped off at any FedEx customer location. A FedEx employee will need to examine the package to determine if it can be transported by FedEx. Retain copies of the shipping forms for shipping documentation.

***Table 13-3: FEDEX Packaging, Marking, and Labeling Requirements***

<b>Packaging Requirements</b>
<ul style="list-style-type: none"> <li>• Package should be in good condition, free of external damage, leakage, or odors.</li> <li>• Package must be permitted by the packing instruction .</li> <li>• If UN specification packaging is used, X (PG I, II, or III), Y (PG II or III), or Z (PG III), it must correspond with the packing group.</li> <li>• Toxics in packing groups I or II (primary or subsidiary risk) - package is DOT Exemption packaging for U.S. domestic or "V-Rated" for international.</li> </ul>
<b>Marking Requirements</b>
<ul style="list-style-type: none"> <li>• Package must be marked with the proper shipping name (and technical name(s) in parentheses for asterisked entries).</li> <li>• Package must be marked with UN or ID number preceded by the prefix "UN" or "ID."</li> <li>• Package must be marked with the name and address of shipper and consignee.</li> </ul> <p><b><u>If Applicable:</u></b></p> <ul style="list-style-type: none"> <li>• If a "Y" packing instruction is used, "Limited Quantity" or "LTD QTY" must be specified.</li> <li>• Netweight of dry ice (in kg) is specified.</li> <li>• The words "Do Not Drop-Handle with Care" on the package. "Keep Upright" must be at 120 degree intervals around the package. Arrows or orientation labels must be affixed. Instructions in the event of emergency, delay, or if shipment remains unclaimed should be included.</li> <li>• When an overpack is indicated on the shipper's declaration, all aspects comply, including: a. the dangerous goods are compatible; b. if UN specification packagings are used, the statement "Inner packages comply with prescribed specifications" is marked on the package.</li> <li>• "RQ" is marked on the package when written on the declaration.</li> <li>• "DOT -E-####" is marked on the package when shipped as a DOT Exemption.</li> </ul>
<b>Labeling Requirements</b>
<ul style="list-style-type: none"> <li>• The correct primary risk label(s) must be used. The number must be indicated on the bottom corner.</li> <li>• The correct subsidiary risk label(s) must be used, if applicable. The number must not be indicated on the bottom corner.</li> <li>• Use a "Cargo Aircraft Only" label (Danger), if applicable.</li> <li>• For liquids in combination packaging and overpacks, two package orientation labels (arrows up) on opposite sides are required (these labels are not required for Class 3 if inner receptacles are 120 ml or less, or for Class 6.2, if inner receptacles are 50 ml or less).</li> <li>• Labels must be correctly applied and not obscured; irrelevant markings/labels must be removed.</li> </ul>

Phone UPS at 800-242-2111 the day before the carton is to be picked up. UPS will visit the same pick-up point each day for the remainder of the week for the one time per week charge, if desired. Initially, an appointment will need to be made with a UPS representative to establish a UPS shipper number.

***Table 13-4: FedEx Dangerous Goods Airbill Instructions***

<b>Shipper's, Payment, and Service Information</b>	
<ul style="list-style-type: none"> <li>• Include the name and address of shipper.</li> <li>• Include the name and address of consignee.</li> <li>• Indicate page of pages.</li> <li>• Under Transport Details, correctly indicate whether item is packed within Passenger or Cargo Aircraft Only limitations.</li> <li>• Under shipment Type, cross out the word "Radioactive."</li> </ul>	
<b>Nature &amp; Quantity of Dangerous Goods</b> (bottom of form)	
<ul style="list-style-type: none"> <li>• Include the proper shipping name (and technical name[s] in parentheses for asterisked entries).</li> <li>• Indicate the Class or Division number(s) (and Class 1, compatibility group).</li> <li>• Indicate the UN or ID number, preceded by the prefix "UN" or "ID."</li> <li>• Include the packing group number, when applicable (i.e., I, II, or III).</li> <li>• Include the subsidiary risk number(s), when applicable, corresponding to the subsidiary risk label(s) applied (step 5).</li> <li>• Indicate the number and type of package(s) (i.e., 1 fibreboard box or 1 4G).</li> <li>• Include the total net quantity per package (must be in metric units).</li> <li>• Indicate the packing instruction number (i.e., 307 or Y419).</li> <li>• Provide authorization information (name and title of signatory, place, and date).</li> <li>• Sign the form.</li> <li>• Under addition shipping information, include the 24-hour emergency response telephone number (not required for magnetized material, consumer commodity, LTD QTY., "Castor" PSNs [all UN 2969]); no beeper or pager numbers should be used.</li> </ul>	
<b><u>If Applicable:</u></b>	
<ul style="list-style-type: none"> <li>• If a "Y" packing instruction is used, "Limited Quantity" or "LTD. QTY" must be specified.</li> <li>• When an overpack is indicated, all aspects must comply, including: a. the dangerous goods must be compatible; and b. if UN specification packagings are used, the statement "Inner packages comply with prescribed specifications" is marked on the package.</li> <li>• When "all packed in one outer package" is indicated on the declaration, the dangerous goods must be compatible and a "Q value" should be listed (not required for dry ice).</li> <li>• Include the shipper's full signature next to amendments or alterations.</li> <li>• The form should indicate "DOT -E-####" in authorization column when shipped as a DOT Exemption. A current copy of the Exemption must travel with the shipment.</li> <li>• "RQ" should be written on the form when marked on the package.</li> </ul>	

Exhibit 13-1: FedEx Dangerous Goods Airbill

**FedEx** Dangerous Goods Airbill **Sender's Copy**  
RETAIN FOR 1 YEAR  
**RETAIN THIS COPY FOR YOUR RECORDS**

*The World On Time*

**1 From** Please print and press hard.  
 Date \_\_\_\_\_ Sender's FedEx Account Number \_\_\_\_\_  
 Sender's Name \_\_\_\_\_ Phone (\_\_\_\_) \_\_\_\_\_  
 Company \_\_\_\_\_  
 Address \_\_\_\_\_ Dept./Floor/Suite/Room \_\_\_\_\_  
 City \_\_\_\_\_ State \_\_\_\_\_ ZIP \_\_\_\_\_

**2 Your Internal Billing Reference** \_\_\_\_\_ OPTIONAL  
 First 24 characters will appear on invoice.

**3 To**  
 Recipient's Name \_\_\_\_\_ Phone (\_\_\_\_) \_\_\_\_\_  
 Company \_\_\_\_\_  
 Address \_\_\_\_\_ We cannot deliver to P.O. boxes or P.O. ZIP codes. Dept./Floor/Suite/Room \_\_\_\_\_  
 City \_\_\_\_\_ State \_\_\_\_\_ ZIP \_\_\_\_\_

**For HOLD at FedEx Location check here**  
 Hold Weekday  Hold Saturday  
Available for FedEx Priority Overnight and FedEx 2Day to select locations.

**For WEEKEND Delivery check here**  
 Saturday Delivery  Sunday Delivery  
Available for FedEx Priority Overnight and FedEx 2Day to select ZIP codes.

**4a Express Package Service Packages up to 150 lbs.** Delivery commitment may be later in some areas.  
 FedEx Priority Overnight Next business morning  FedEx Standard Overnight Next business afternoon  
 FedEx 2Day Second business day  FedEx Express Saver Third business day

**4b Express Freight Service Packages over 150 lbs.** Delivery commitment may be later in some areas.  
 FedEx 1Day Freight\* Next business day  FedEx 2Day Freight Second business day  FedEx 3Day Freight Third business day  
 \* Call for Confirmation: \_\_\_\_\_

Service Conditions, Declared Value, and Limit of Liability - By using this Airbill, you agree to the service conditions in our current Service Guide or U.S. Government Service Guide. Both are available on request. SEE BACK OF SENDER'S COPY OF THIS AIRBILL FOR INFORMATION AND ADDITIONAL TERMS. We will not be responsible for any claim in excess of \$100 per package whether the result of loss, damage, delay, non-delivery, modification, or misinformation, unless you declare a higher value, pay an additional charge, and document your actual loss in a timely manner. Your right to recover from us for any loss includes intrinsic value of the package, loss of sales, interest, profit, attorney's fees, costs, and other forms of damage, whether direct, incidental, consequential, or special, and is limited to the greater of \$100 or the declared value but cannot exceed actual documented loss. The maximum declared value for any FedEx Letter and FedEx Pak is \$500. Federal Express may, upon your request, and with some limitations, refund all transportation charges paid.  
 See the FedEx Service Guide for further details.

**Questions? Call 1•800•Go•FedEx® (800-463-3339) or Visit our Web site at www.fedex.com**

**5 Packaging**  
 Other Packaging  
 Dangerous Goods cannot be shipped in FedEx packaging.

**6 Special Handling**  
 Dangerous Goods as per attached Shipper's Declaration  Cargo Aircraft Only

**7 Payment**  
 Bill to:  Sender Acc. No. in Section 1 will be billed  Recipient  Third Party  Credit Card  Cash/Check  
Enter FedEx Acct. No. or Credit Card No. below

FedEx Account No. \_\_\_\_\_  
 Credit Card No. \_\_\_\_\_ Exp. Date \_\_\_\_\_  

Total Packages	Total Weight	Total Declared Value*
		\$ .00

\* When declaring a value higher than \$100 per shipment, you pay an additional charge. See SERVICE CONDITIONS, DECLARED VALUE, AND LIMIT OF LIABILITY sections for further information.

**Signature Release Unavailable** PART 4154828 • Rev. Date 11/99 ©1994-98 FedEx • PRINTED IN U.S.A.

FedEx Tracking Number **811508905478** Form I.D. No. **0204** 374

Page 1 of 1 Pages

Two completed and signed copies of this Declaration must be handed to the operator.

**TRANSPORT DETAILS**  
 This shipment is within the limitations prescribed for: (delete non-applicable)  
 PASSENGER AND CARGO AIRCRAFT  CARGO AIRCRAFT ONLY  
 Airport of Departure: \_\_\_\_\_  
 Airport of Destination: \_\_\_\_\_

**WARNING**  
 Failure to comply in all respects with the applicable Dangerous Goods Regulations may be in breach of the applicable law, subject to legal penalties. This Declaration must not, in any circumstances, be completed and/or signed by a consolidator, a forwarder or an IATA cargo agent.  
 Shipment type: (delete non-applicable)  
 NON-RADIOACTIVE  RADIOACTIVE

NATURE AND QUANTITY OF DANGEROUS GOODS					Quantity and Type of Packaging	Packing Instr.	Authorization
Dangerous Goods Identification							
Proper Shipping Name	Class or Division	UN or I.D. No.	Packing Group	Subsidiary Risk			
FOR SHIPMENTS WITHIN USA, AK, AND HI ONLY							

**Additional Handling Information** \_\_\_\_\_ **Prepared for AIR TRANSPORT according to:** (Customer MUST check one)  
 49 CFR  ICAO / IATA

I hereby declare that the contents of this consignment are fully and accurately described above by the proper shipping name and are classified, packaged, marked, and labeled/placarded, and are in all respects in proper condition for transport according to applicable international and national governmental regulations.  
 Emergency Telephone Number (Required for U.S. Origin or Destination Shipments) \_\_\_\_\_  
 Name/Title of Signatory \_\_\_\_\_  
 Place and Date \_\_\_\_\_  
 Signature (see warning above) \_\_\_\_\_

IF ACCEPTABLE FOR PASSENGER AIRCRAFT, THIS SHIPMENT CONTAINS RADIOACTIVE MATERIAL INTENDED FOR USE IN, OR INCIDENT TO, RESEARCH, MEDICAL DIAGNOSIS, OR TREATMENT.